

Carbon Nanomaterial Produced by Microwave Exfoliation of Graphite Oxide

Y.M. Shulga^{1,*}, S.A. Baskakov¹, E.I. Knerelman¹, G.I. Davidova¹, E.R. Badamshina¹,
N.Y. Shulga², E.A. Skrileva², A.L. Agapov³, D.N. Voylov^{3,1}, A.P. Sokolov^{3,4}

¹ *Institute of Problems of Chemical Physics RAS, 142432 Chernogolovka, Moscow region, Russian Federation*

² *National University of Science and Technology MISiS, 117936 Moscow, Russian Federation*

³ *Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996-1600, USA*

⁴ *Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*

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Carbon-based graphene-like material was obtained through microwave stimulated exfoliation of graphite oxide (GO). Properties of this material were investigated by multiple techniques including element analysis, X-ray photoelectron spectroscopy (XPS), mass-spectroscopy, infrared (IR) and Raman spectroscopy, scanning electron microscopy (SEM) and broadband dielectric spectroscopy. Specific surface area and volume of microwave exfoliated graphite oxide (MEGO) reached 600 m²/g and 6 cm³/g, respectively. It is shown that during such explosive reduction process the sample emits CO₂, CO and H₂O and, in some cases, SO₂ gases. The resulting reduced material exhibits IR spectra similar to that of graphite and a dc-conductivity of 0.12 S/cm. It is also shown that prolonged storage in ambient conditions leads to elevated oxygen content and decrease of specific surface area of the samples.

Keywords: XPS, IR-spectroscopy, 3d graphene, Specific surface, Electrical conductivity.

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1. INTRODUCTION

It was reported that a conductive microwave exfoliated graphite oxide (MEGO) can be produced by a short-term microwave treatment of graphite oxide synthesized by Hammers method [1]. The as-prepared MEGO shows relatively high specific surface area (SSA) of 463 m²/g and a decent conductivity of 274 S/m [1]. Later, same laboratory have demonstrated that this relatively cheap MEGO can be used as a precursor material in the manufacturing process of a chemically activated MEGO (a-MEGO) [2]. The a-MEGO material possesses SSA of 3100 m²/g and conductivity of 500 S/m and can be directly used as an electrode material to produce ultracapacitors with remarkably high specific capacitance of 200 F/g.

Recently, another interesting use of MEGO was found in our laboratory. It was found that irradiation of tetrafluoroethylene, C₂F₄, and MEGO mixture by gamma rays at the temperature of liquid nitrogen leads to high-yield formation of a composite with a significant percentage of polytetrafluoroethylene (PTFE), about 80 wt % [3]. It was shown that MEGO plays a role of an initiator of C₂F₄ low-temperature polymerization process since polymerization of C₂F₄ at the same conditions, but without MEGO decreases the yield of PTFE in 6 times. The resulting PTFE-MEGO composite shows promise as a basis for creating products with a low flowability and increased wear resistance in comparison to pure PTFE.

Therefore, further analysis of MEGO properties and its processing is important from the point of view of its use as independent lightweight carbon-based mesoscale filler and in subsequent synthesis of a-MEGO for use as electrode material in ultracapacitors. In the current manuscript we examine in detail the formation process

and properties of MEGO. Microwave treatment of graphite oxide leads to the formation of a conductive carbon material with a specific surface area of about 600 m²/g. The microwave reduction of graphene oxide is accompanied by a thermal explosion and a release of various gases. It is shown that the gaseous products of such explosive reduction process are mostly CO₂, CO and H₂O and, in some cases, SO₂. The MEGO material obtained in such a way exhibits IR spectra similar to that of graphite and reasonably high conductivity value of 0.12 S/cm. It is also shown that MEGO sample are metastable materials at ambient conditions. Prolonged storage in regular air atmosphere at room temperature leads to increase of oxygen content and decrease of specific surface area of the samples.

2. EXPERIMENTAL TECHNIQUE

Graphite oxide (GO) has been synthesized using Hammers method [4]. GO film of about 1 cm² was placed in a deep quartz vessel, the open part of which was covered with a filter of cotton fabric, designed to capture the explosion products. Then the quartz vessel was placed into a microwave oven (2450 MHz, 900 W) and conducted heating till the explosion, after which the heating was stopped. To determine the composition of the gases released by the explosion, the film was placed in a quartz tube with a vacuum up to 3×10^{-7} Torr. After degassing, the vessel with the GO film was placed in a microwave oven and heated to the explosion. After cooling to a room temperature the vessel was combined through a vacuum faucet with an inlet of the mass spectrometer for analysis.

“Elementar Vario Cube” analyzer was used to determination of C, H, O content. Specific surface area measurements were performed using low temperature

* shulga@icp.ac.ru

adsorption with Autosorb-1 (Quantachrome Corp.) equipment. IR spectra were measured in the range of 4000-670 cm^{-1} using Fourier spectrometer Perkin Elmer Spectrum 100 with the UATR module. X-ray photoelectron spectroscopy was performed by PHI-5500. A non-monochromatized Mg K α X-ray source was used ($h\nu = 1253.6 \text{ eV}$) with power of 300 W. Scanned area was about 1.2 mm^2 . The base pressure in the sample chamber did not exceed 1×10^{-9} Torr. Analysis of gases produced by the explosion of GO film in a vacuum, was performed using a mass spectrometer MI 1201V. Ionization of the gas was carried by an electron beam with an energy of 70 eV. Mass spectra were recorded in the interval $1 \leq m/z \leq 250$, where m – the atomic weight, z – ion charge. Micrographs of the samples were obtained using a scanning electron microscope Zeiss LEO SUPRA 25. Raman scattering (RS) was excited by laser ($\lambda = 976 \text{ nm}$) and recorded with the NXT FT-Raman 9650 device.

3. RESULTS

Microwave treatment essentially reduces content of oxygen (from 44.8 to 4.2 wt. %) and hydrogen (from 2.7 to 0.7 wt %) in sample. Meanwhile the SSA dramatically increases (from 20 to 600 m^2/gr).

The adsorption desorption isotherm for MEGO is characteristic for mesoporous samples. The hysteresis on the adsorption desorption isotherm refers to the so-called H3 type on IUPAC classification [5] and points to presence of a slot-like pore or plane-parallel particles.

On the Fig. 1 (curve 1) the IR spectrum of initial GO is presented. The received spectrum coincides with that, received in work [6], but differs from the spectra received by authors [7-8] by considerably smaller intensity of absorption band (AB) at 980-930 cm^{-1} . This AB is usually connected with fluctuations of epoxy groups. At a range of 3000-3700 cm^{-1} there is a number of overlapping AB which, according to literature data, can attribute valence fluctuations of O-H bond. Absorption band at 1730 cm^{-1} can be attributed to C=O valence fluctuations in carbonyl groups and/or ketones. AB at 1620 cm^{-1} is naturally can be attributed to deformation fluctuations of water molecules, and close AB at 1590 cm^{-1} – to the allowed fluctuations of basal plane rings.

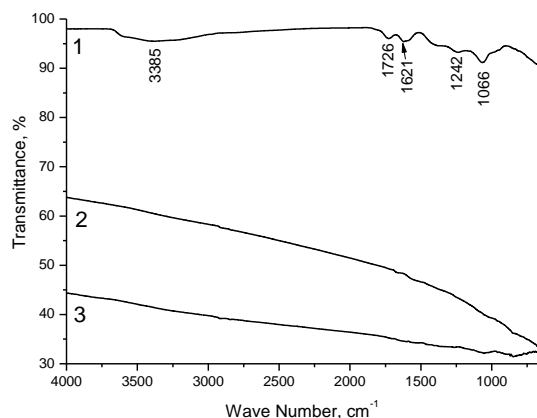


Fig. 1 – IR spectra of GO (1), MEGO (2), and graphite (3)

According to the literature data, AB at 1360-1380 cm^{-1} is connected with fluctuation of C-OH bond, at 1220-1230 cm^{-1} – with fluctuations of C-O-C group and at 1060-1080 cm^{-1} – with phenylhydroxyl groups. After GO processing in the microwave oven (MEGO) all peaks characteristic for GO disappeared in the spectrum (curve 2). We believe that it is connected with increase in conductivity of a sample as the MEGO spectrum comes nearer to a graphite spectrum on its form (curve 3).

XPS spectra in C1s region of GO and MEGO are presented in Fig. 2. The C1s spectrum of GO is well approximated by three Gaussians. According to literature data [9-14], the peak with $E_{\text{c}} = 285 \text{ eV}$ is caused by carbon atoms in which immediate environment there are only other atoms of carbon. The second peak (287 eV) the majority of authors connect with carbon atoms having one bonded oxygen atom, i.e. with epoxy (>C-O-C<) and/or hydroxyl (>C-OH) groups. Appearance of third peak is attributed to carbon atoms with two bonded oxygen atoms. Comparing intensities of separate peaks, it is possible to say that 57 % of carbon atoms of initial GO are connected with one oxygen atom, and 8 % – with two oxygen atoms.

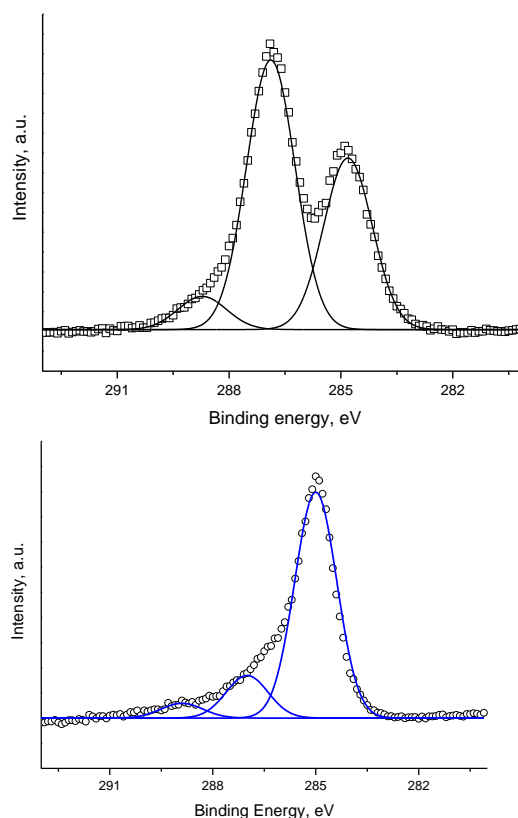


Fig. 2 – XPS spectra of C1s regions of GO (top image) and MEGO (bottom image)

C1s spectrum of MEGO differs from that for initial GO. Decomposition on separate components showed that in MEGO only 15 % of carbon atoms are connected with one oxygen atom and 5 % – with two carbon atoms. Thus, processing of OG film connected with described heating in the microwave oven is accompanied by essential increase of a part of carbon atoms which

aren't bonded with oxygen atoms. The relation of integral intensities of I (O1s)/I (C1s) at transition from GO to MEGO decreased in 4.5 times.

Mass-spectrometer research gases composition, forming at explosion of graphite oxide film, showed (Fig. 3) that the main components of a gas mixture are carbon oxides CO ($m/z = 28$) and CO₂ ($m/z = 44$). Taking into account that in the mass spectrum of pure CO₂ intensity of peak with $m/z = 28$ (ions [CO]⁺) makes about 40 % from intensity of peak with $m/z = 44$ (ions [CO₂]⁺), it is possible to say that in a gas phase seven molecules of CO related to 10 molecules of CO₂. Besides carbon oxides, the GO sample produces in a gas phase also water (peak with $m/z = 18$). As to molecular oxygen, it is practically absent in a gas phase. From the unexpected results received at research of mass spectra, it is necessary to note reliably established production of SO₂ molecules in a gas phase (peaks with $m/z = 48$ (ions [SO]⁺) and with $m/z = 64$ (ions [SO₂]⁺). Formation of molecules we connect with the remains of sulfuric acid used by receiving GO. From mass spectrometer researches follows that at explosion, stimulated by microwave oven heating, occurs not only GO restoration, but also cleaning from sulfuric remains.

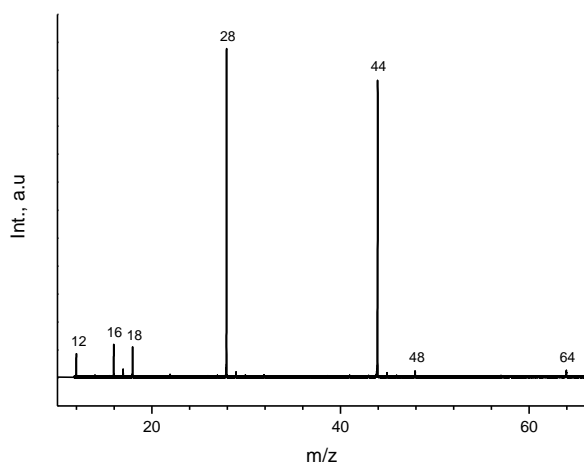


Fig. 3 – Mass-spectra of gases forming at explosion of graphite oxide film in vacuum

The microphotos received by scanning electronic microscopy are shown in Fig. 4. At initial GO the flat particles formed by the parallel planes of graphene oxide are visible. After explosive processing planes of the restored graphene oxide are warped that keeps them from a collapse and provides a high specific surface of MEGO.

Conductivity spectrum of MEGO sample can be seen on Fig. 5. The absolute value of conductivity was determined to be 0.121 S/cm. Such conductivity value is several significantly lower than the electrical conductance of compacted graphite [15, 16]. Microwaved GO shows rather low conduction properties even if one takes into account that in present study conductivity was measured along the compaction direction (lower conductivity due to preferential orientation of flakes). One of the possible reasons that microwaved GO showed poor conductivity performance could be oxida-

tion MEGO in course of air storage (see above). Nevertheless, conductivity value of 0.121 S/cm is reasonable for many applications.

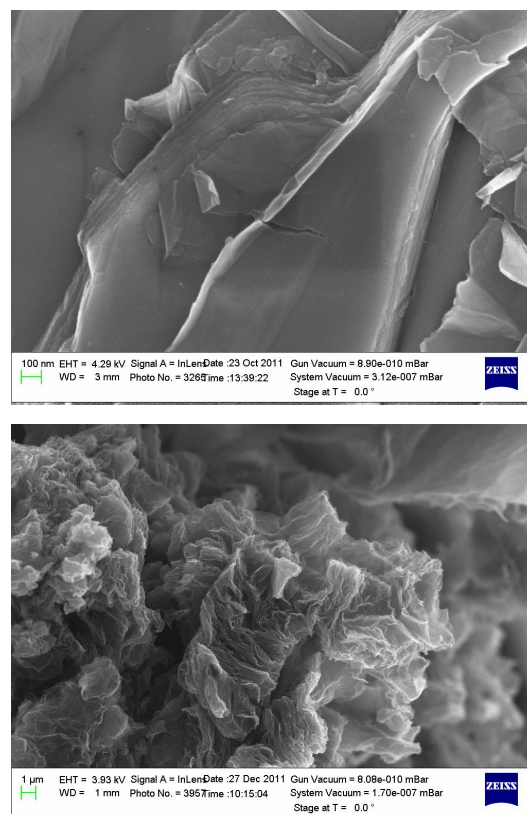


Fig. 4 – Microphotographies of GO (top) and MEGO (bottom)

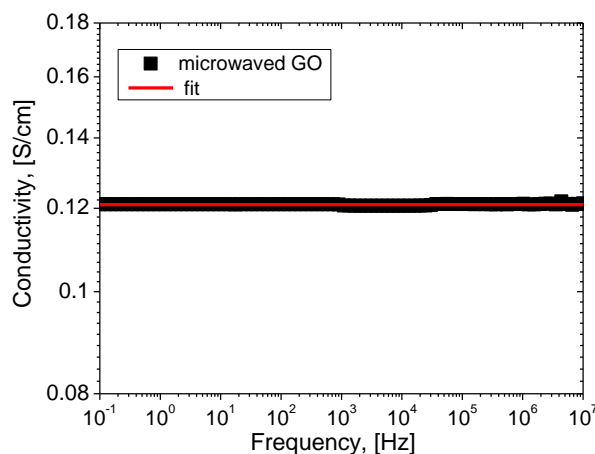


Fig. 5 – Conductivity spectrum of MEGO

Thus ease of production, high surface area and good dispersability in polymeric media makes microwave-reduced GO an industrially relevant material.

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REFERENCES

1. Y. Zhu, S. Murali, M.D. Stoller, et al., *Carbon*, **48**, 2118 (2010).
2. Y. Zhu, S. Murali, M.D. Stoller, et al., *Science*, **332**, 1537 (2011).
3. Y.M. Shulga, S.A. Baskakov, D.P. Kiryukhin, et al., *High Energy Chem.* **47**, 73 (2013).
4. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* **80**, 1339 (1958).
5. *Adsorption, Surface Area and Porosity* (S.J. Gregg, K.S.W. Sing) (Academic Press: London: 1982).
6. Y. Si, E.T. Samulski, *Nano Lett.* **8**, 1679 (2008).
7. H.-K. Jeong, Y.P. Lee, M.H. Jin, et al., *Chem. Phys. Lett.* **470**, 255 (2009).
8. L.J. Cote, R. Cruz-Silva, J. Huang, *J. Am. Chem. Soc.* **131**, 11027 (2009).
9. T. Szabo, O. Berkesi, P. Forgo, et al., *Chem. Mater.* **18**, 2740 (2006).
10. J.R. Lomeda, C.D. Doyle, D.V. Kosynkin, et al., *J. Am. Chem. Soc.* **130**, 16201 (2008).
11. C. Xu, X. Wang, J. Zhu, *J. Phys. Chem. C* **112**, 19841 (2008).
12. S. Park, K.-S. Lee., G. Bozoklu, et al., *ACS Nano*. **2**, 572 (2008).
13. J.I. Paredes, S. Villar-Rodil, P. Solis-Fernandez, et al., *Langmuir*. **25**, 5957 (2009).
14. C. Shan, H. Yang, J. Song, et al., *Anal. Chem.* **81**, 2378 (2009).
15. N. Deprez, D.S. McLachlan, *J. Phys. D: Appl. Phys.* **21**, 101 (1988).
16. A. Celzard, J.F. Maréché, G. Furdin, et al., *J. Phys. D: Appl. Phys.* **33**, 3094 (2000).